oxygen–acceptor oxygen distance of 2.663 (4) Å (Fitzgerald, Gallucci & Gerkin, 1991), is compared with the present case.

A unit cell for the tetragonal phase of 1,2-naphthalenedicarboxylic acid containing diethyl ether is shown in Fig. 4 and a unit cell of the triclinic phase of the diacid is shown in Fig. 5. For the tetragonal unit cell, infinite helical chains form about each fourfold screw axis as a result of the hydrogen bonding at the C(1) position as described above. These chains parallel to the z direction are interconnected through cyclic dimer hydrogen bonding at the C(2) position. This framework results in open channels parallel to c, the walls of which are composed principally of naphthalene rings. Within these channels are solvent molecules, in this case, disordered diethyl ether molecules. The channels are also the location of the $\bar{4}$ sites, which virtually assures that solvent molecules will be incompatible with the site symmetry even if they are at fixed locations within the channel. In Fig. 4, the partial-occupancy C atoms used to account for the electron density along the columns parallel to c and through the $\bar{4}$ sites are drawn to illustrate the presence of the disordered solvent in the channels. In the triclinic unit cell (Fig. 5), intermolecular hydrogen bonding occurs across inversion centers at both carboxylic acid positions, producing a cyclic dimer at the C(1) position nearly perpendicular to the naphthalene ring and a cyclic dimer at the C(2) position nearly co-planar with the naphthalene ring. This arrangement produces infinite ribbons of molecules hydrogen bonded in a zigzag pattern and overlapped in such a manner as to occupy the space created above and below the naphthalene rings by the carboxylic acid dimers at the C(1) positions.

The support of LJF by PPG Industries is gratefully acknowledged. Partial support of this research through the purchase of the diffractometer system by an NIH grant is also gratefully acknowledged.

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Structures of Three Biologically Active Conjugates of ω-Amino Acids and Plant Growth Hormone (Auxin)

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(*Received* 17 *September* 1991; *accepted* 27 *November* 1991)

Abstract

The crystal structures of biologically active conjugates of the plant growth hormone, indole-3-acetic acid (IAA = auxin) with the non-natural ω-amino acids β-alanine (1), γ-aminobutyric acid (2) and ε-aminohexanoic (ε-aminocaproic) acid (3) have been determined. (1) *N*-(IAA)-β-Ala, $C_{13}H_{14}N_2O_3$, M_r = 246.27, orthorhombic, *Pbca*, a = 9.114 (2), b = 23.933 (4), c = 11.034 (4) Å, V = 2406.8 (9) Å^3, Z = 8, D_x = 1.359 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0.71073 Å, μ = 0.92 cm^{-1}, $F(000)$ = 1040, T =

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0108-7681/92/030297-06$06.00

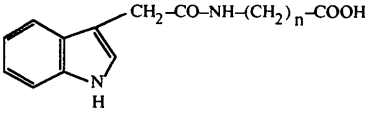
133 K, $R = 0.036$, $wR = 0.039$ for 1557 reflections with $I \geq 3\sigma(I)$. (2) *N*-(IAA)-γ-Abu, $C_{14}H_{16}N_2O_3$, $M_r = 260.29$, orthorhombic, $P2_12_12_1$, $a = 5.072$ (1), $b = 10.307$ (3), $c = 24.856$ (4) Å, $V = 1299.3$ (4) Å^3, $Z = 4$, $D_x = 1.331$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.88$ cm^{-1}, $F(000) = 552$, $T = 298$ K, $R = 0.030$, $wR = 0.036$ for 1085 reflections with $I \geq 3\sigma(I)$. (3) *N*-(IAA)-ε-Ahx, $C_{16}H_{20}N_2O_3$, $M_r = 288.35$, triclinic, $P\bar{1}$, $a = 9.058$ (3), $b = 9.693$ (5), $c = 9.843$ (5) Å, $\alpha = 102.07$ (6), $\beta = 104.36$ (5), $\gamma = 107.02$ (7)°, $V = 762.6$ (9) Å^3, $Z = 2$, $D_x = 1.256$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 6.74$ cm^{-1}, $F(000) = 308$, $T = 298$ K, $R = 0.048$, $wR = 0.058$ for 2131 reflections with $I \geq 3\sigma(I)$. The common structural feature of the indole moiety is the closure of the C6—C7—C71 angle to 117.2 (2)°. The indole ring system and C atom of the adjacent methylene group are coplanar. The CH_2–carbonyl bond is approximately perpendicular to this plane. In the structures (1) and (3) the peptide O atom points away from the indole ring whereas in (2) the torsion angle C3—C8—C9—O9 is 45.1 (4)°. The orientations of the amino-acid chains with respect to the aromatic rings are also different. However, the conformation of the indole moiety and the two adjacent C atoms is identical for the structures described. Thus the indole NH group is not sterically blocked and remains available for interactions with proteins of specific enzymes.

Introduction

Indole-3-acetic acid (IAA) is a plant growth hormone (auxin) which regulates many physiological functions including cell division and enlargement, developmental differentiation, and the synthesis of specific proteins (Davies, 1987). Bound auxins, or auxin conjugates (Cohen & Bandurski, 1982; Magnus, 1987) are involved in hormone transport and serve as long- and short-term storage forms of hormone. Molecular recognition of auxin and its biologically active conjugates has been studied (Kojić-Prodić, Nigović, Horvatić *et al.*, 1991; Duddeck, Hiegemann, Simeonov, Kojić-Prodić, Nigović & Magnus, 1989). Crystal structures of *N*-indol-3-ylacetyl derivatives (IAA conjugates) of aliphatic amino acids including α-L-amino and ω-amino acids have been solved. The influence of conformational changes of auxins on their biological activity has been studied by molecular mechanics and dynamics. Some of the conjugates studied involve amino acids which have not been known as protein constituents. However, they were prepared, chemically characterized and tested as sources of auxin in plant tissue culture (Magnus, Hangarter & Good, 1992; Magnus, Nigović, Hangarter & Good, 1992). Four members of the ω-amino-acid series (see scheme below) are biologically active (Kojić-Prodić, Nigović, Horvatić, Ružić-Toroš & Magnus, 1990). Crystal structure determinations of *N*-(IAA)-β-Ala, *N*-(IAA)-γ-Abu and *N*-(IAA)-ε-Ahx are described in this paper. The crystal structure of *N*-(IAA)-δ-aminovaleric acid [*N*-(IAA)-δ-Ava] has already been reported (Kojić-Prodić, Nigović, Horvatić *et al.*, 1991).

Table 1. *Details of data collection and refinement*

	N-(IAA)-β-Ala (1)	*N*-(IAA)-γ-Abu (2)	*N*-(IAA)-ε-Ahx (3)
Crystal size (mm)	0.45 × 0.30 × 0.30	0.36 × 0.28 × 0.14	0.40 × 0.29 × 0.28
No. of reflections used for cell parameters and θ range (°)	25 7–18	25 7–16	25 7–18
θ range for intensity measurement (°)	2–25	2–25	2–25
hkl range	0,10; 0,28; 0,13	0,6; 0,12; 0,29	−11,10; −11,11; 0,1
ω scan width	0.7 + 0.35tanθ	0.8 + 0.35tanθ	0.8 + 0.35tanθ
No. of measured reflections (unique)	2439	1385	2567
No. of reflections with $I \geq 3\sigma(I)$	1557	1085	2131
No. of parameters	219	236	255
R	0.036	0.030	0.048
wR, $w^{-1} = k[\sigma(F_o)^2 + g(F_o)]$	0.039	0.036	0.058
k, *g*	1.856, 0.0005	0.4507, 0.0005	1.000, 0.005
Final shift/e.s.d.	0.079 (C9, *x*)	0.025 (C3, *y*)	0.342 (C6, *y*)
Residual electron density $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.24, −0.26	0.11, −0.14	0.16, −0.26



N-(IAA)-β-Ala $n = 2$
N-(IAA)-γ-Abu $n = 3$
N-(IAA)-δ-Ava $n = 4$
N-(IAA)-ε-Ahx $n = 5$

Experimental

Conjugates of the ω-amino acids were prepared by aminolysis of *N*-(indol-3-ylacetoxy)succinimide (Magnus, Nigović, Hangarter & Good, 1992), a method originally used by Fuchs, Haimovich & Fuchs (1971), to synthesize *N*-(IAA)-ε-Ahx. Crystals of *N*-(IAA)-β-Ala were obtained from ethanol after 3 days at 275 (2) K. Crystals of *N*-(IAA)-γ-Abu were grown from ethyl acetate and benzene (1:2 *v*/*v*) over 15 days at 275 (2) K. Crystals of *N*-(IAA)-ε-Ahx were prepared from the same solvent mixture, but in a ratio of 1:1, over 6 days at 275 (2) K. Details of data collection and refinement are listed in Table 1.

The compounds studied have no chiral centers and normally crystallize in centrosymmetric space groups except for *N*-(IAA)-γ-Abu which adopts $P2_12_12_1$. Intensity data were collected on an Enraf–Nonius CAD-4F diffractometer with graphite-monochromatized radiation (Table 1). The measurement was carried out at 133 K for *N*-(IAA)-β-Ala and at room-temperature for *N*-(IAA)-γ-Abu and *N*-(IAA)-

ε-Ahx. No significant intensity variations for standard reflections were observed. Data were corrected for Lorentz and polarization effects using the Enraf–Nonius *SDP/VAX* package (B. A. Frenz & Associates Inc., 1982). Structures were solved by *SHELX*86 (Sheldrick, 1985). Refinement was by full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ with the *SHELX*77 system of programs (Sheldrick, 1983) using F values. The H-atom coordinates were determined from successive difference Fourier syntheses for structures (1) and (2). For structure (3) the H atoms attached to C23 and C22 of the side chain and C5 of benzene ring were calculated on stereochemical grounds and refined riding on their respective C atoms. In the structures (1), (2) and (3) the N22—H bond distances were normalized to the values obtained by neutron diffraction (N—H, 1.009 Å). The O—H distance in structure (1) and N1—H in (2) were also normalized. The non-H atoms were refined anisotropically; details of the refinement procedures are listed in Table 1. Scattering factors are those included in *SHELX*77 (Sheldrick, 1983). Molecular geometry was calculated by the program package *EUCLID* (Spek, 1982). Drawings were prepared by the program *PLUTON* incorporated in *EUCLID* and *ORTEP*II (Johnson, 1976). The final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.* Calculations were performed on MicroVAX II and IRIS-4D25G computers of the X-ray Laboratory, Ruder Bošković Institute, Zagreb.

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters* ($\times 10^4$)

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq} (Å^2)
N-(IAA)-β-Ala (1)				
N1	0.6884 (2)	0.6307 (1)	0.0173 (1)	227 (5)
C2	0.6988 (2)	0.5848 (1)	0.0912 (2)	210 (6)
C3	0.7918 (2)	0.5955 (1)	0.1858 (2)	192 (5)
C31	0.8433 (2)	0.6520 (1)	0.1694 (2)	197 (6)
C4	0.9409 (2)	0.6863 (1)	0.2343 (2)	224 (6)
C5	0.9691 (2)	0.7393 (1)	0.1901 (2)	280 (6)
C6	0.9027 (2)	0.7585 (1)	0.0831 (2)	295 (6)
C7	0.8061 (2)	0.7259 (1)	0.0179 (2)	264 (6)
C71	0.7775 (2)	0.6725 (1)	0.0625 (2)	206 (6)
C8	0.8364 (2)	0.5566 (1)	0.2849 (2)	210 (6)
C9	0.7970 (2)	0.5730 (1)	0.4128 (2)	191 (5)
O9	0.8591 (2)	0.5499 (1)	0.4997 (1)	253 (4)
N22	0.6912 (2)	0.6107 (1)	0.4281 (1)	219 (5)
C22	0.5335 (2)	0.5801 (1)	0.5960 (2)	220 (6)
C23	0.6338 (2)	0.6256 (1)	0.5474 (2)	234 (6)
C21	0.4928 (2)	0.5891 (1)	0.7257 (2)	203 (5)
O211	0.3972 (2)	0.5519 (1)	0.7669 (1)	289 (5)
O212	0.5432 (2)	0.6262 (1)	0.7883 (1)	283 (4)
N-(IAA)-γ-Abu (2)				
N1	0.7703 (5)	1.3817 (3)	0.8989 (1)	539 (9)
C2	0.8799 (7)	1.2786 (3)	0.9247 (1)	500 (9)
C3	1.0755 (5)	1.2256 (3)	0.8947 (1)	401 (7)
C31	1.0906 (5)	1.3013 (2)	0.8464 (1)	384 (7)
C4	1.2529 (6)	1.2994 (3)	0.8012 (1)	483 (9)
C5	1.2178 (7)	1.3917 (3)	0.7620 (1)	573 (10)
C6	1.0204 (7)	1.4853 (3)	0.7660 (1)	557 (10)
C7	0.8559 (7)	1.4902 (3)	0.8099 (1)	523 (10)
C71	0.8939 (6)	1.3980 (2)	0.8504 (1)	431 (9)
C8	1.2359 (6)	1.1078 (3)	0.9075 (1)	427 (10)
C9	1.1265 (5)	0.9851 (2)	0.8826 (1)	342 (7)
O9	0.8867 (4)	0.9594 (2)	0.8845 (1)	414 (6)
N22	1.3014 (5)	0.9050 (2)	0.8609 (1)	374 (7)
C22	1.1684 (6)	0.6795 (3)	0.9351 (1)	410 (8)
C23	1.3245 (6)	0.6724 (3)	0.8836 (1)	399 (8)
C24	1.2403 (6)	0.7742 (3)	0.8429 (1)	410 (8)
C21	1.2714 (5)	0.5947 (3)	0.9793 (1)	410 (8)
O211	1.1444 (4)	0.6105 (2)	1.0248 (1)	554 (7)
O212	1.4575 (6)	0.5225 (2)	0.9753 (1)	725 (9)
N-(IAA)-ε-Ahx (3)				
N1	0.4837 (2)	0.4430 (2)	0.7492 (2)	505 (4)
C2	0.6261 (2)	0.5045 (2)	0.8650 (2)	479 (4)
C3	0.6371 (2)	0.4076 (2)	0.9454 (2)	409 (4)
C31	0.4900 (2)	0.2760 (2)	0.8745 (2)	391 (4)
C4	0.4285 (3)	0.1375 (2)	0.9021 (2)	496 (4)
C5	0.2807 (3)	0.0313 (2)	0.8063 (3)	607 (5)
C6	0.1926 (3)	0.0605 (3)	0.6840 (3)	614 (4)
C7	0.2475 (2)	0.1958 (3)	0.6558 (2)	552 (5)
C71	0.3973 (2)	0.3023 (2)	0.7522 (2)	431 (5)
C8	0.7742 (2)	0.4295 (2)	1.0792 (2)	473 (5)
C9	0.8772 (2)	0.3332 (2)	1.0583 (2)	406 (4)
O9	0.9716 (2)	0.3205 (2)	1.1649 (2)	599 (4)
N22	0.8595 (2)	0.2646 (2)	0.9206 (2)	473 (4)
C26	0.9387 (2)	0.1592 (2)	0.8768 (3)	531 (4)
C25	0.8241 (2)	−0.0048 (2)	0.8298 (2)	491 (5)
C24	0.6717 (2)	−0.0416 (2)	0.7008 (2)	474 (5)
C23	0.5535 (2)	−0.2051 (2)	0.6519 (2)	492 (5)
C22	0.4014 (3)	−0.2308 (2)	0.5267 (2)	545 (5)
C21	0.2811 (3)	−0.3908 (2)	0.4642 (2)	489 (4)
O211	0.1564 (2)	−0.4065 (2)	0.3511 (2)	684 (4)
O212	0.2956 (2)	−0.4951 (2)	0.5066 (2)	710 (4)

Discussion

The molecular structures of conjugates (1), (2) and (3) with atom numbering are shown in Figs. 1, 2 and 3. The *ORTEP* plots (Johnson, 1976) are drawn with thermal ellipsoids at the 50% probability level. Bond distances and angles are listed in Table 3. The conformations are shown in a superposition diagram (Fig. 4) and Table 4. The crystal packings of the structures (1), (2) and (3), dominated by hydrogen bonds, are given in Figs. 5, 6 and 7 and Table 5.

Statistical analysis of 13 structure determinations of amino-acid conjugates of indol-3-ylacetic acid (Kojić-Prodić, Nigović, Tomić & Danilović, 1991) including the present compounds, reveals shortening of the C6—C7 bond to a mean value of 1.373 (7) Å and closure of the angle C6—C7—C71 to a mean value of 117.4 (5)°, a common feature of indole structures. Bond lengths and angles (Table 3) are comparable at the level of 3σ.

The overall conformation, with respect to the orientation of the indole plane and the side chain, shows two distinctive shapes; the side chain is either folded over the indole ring [*N*-(IAA)-ε-Ahx (3), Fig. 3] or the aliphatic amino-acid chain is extended away from it [*N*-(IAA)-β-Ala (1), Fig. 1; *N*-(IAA)-δ-Ava, Fig. 4]. The molecular conformation of *N*-(IAA)-γ-Abu (2) reveals the variation in the orientation of the carbonyl group at C9 (Fig. 2). However, the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54842 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0111].

conformation for the C2—C3—C8—C9 moiety remains the same for the α-amino-acid and ω-amino-acid conjugates (Kojić-Prodić, Nigović, Horvatić *et al.*, 1991; Table 4 and Fig. 4); the C8—C9 bond is nearly perpendicular to the indole ring plane.

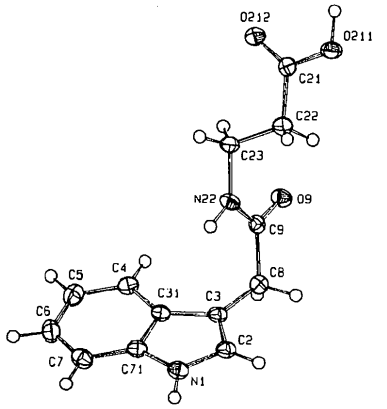


Fig. 1. Molecular structure of *N*-(IAA)-β-Ala (1) with atom numbering.

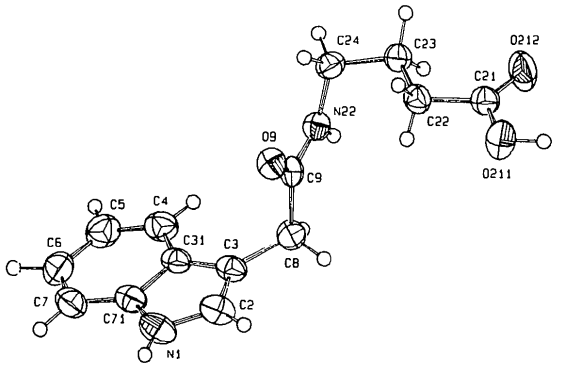


Fig. 2. Molecular structure of *N*-(IAA)-γ-Abu (2) with atom numbering.

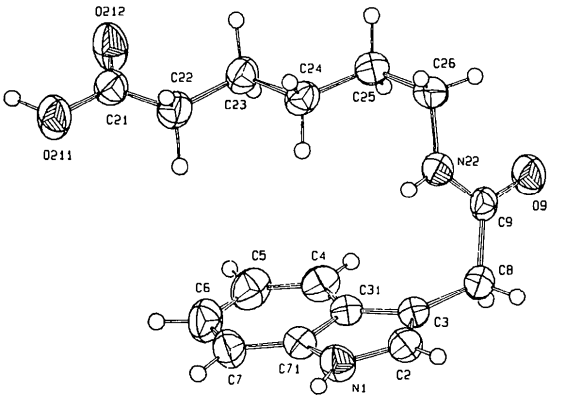


Fig. 3. Molecular structure of *N*-(IAA)-ε-Ahx (3) with atom numbering.

Table 3. *Bond lengths* (Å) *and angles for N-(IAA)-β-Ala* (1), *N-(IAA)-γ-Abu* (2) *and N-(IAA)-ε-Ahx* (3)

	(1)	(2)	(3)
N1—C2	1.371 (3)	1.360 (4)	1.362 (2)
N1—C71	1.382 (3)	1.369 (4)	1.370 (3)
C2—C3	1.369 (3)	1.356 (4)	1.358 (3)
C3—C31	1.443 (3)	1.434 (4)	1.436 (2)
C3—C8	1.492 (3)	1.496 (4)	1.496 (3)
C31—C4	1.406 (3)	1.393 (4)	1.406 (3)
C31—C71	1.411 (3)	1.414 (4)	1.404 (3)
C4—C5	1.383 (3)	1.373 (4)	1.379 (3)
C5—C6	1.404 (3)	1.394 (5)	1.401 (4)
C6—C7	1.379 (3)	1.375 (4)	1.372 (4)
C7—C71	1.394 (3)	1.398 (4)	1.392 (2)
C8—C9	1.508 (3)	1.513 (4)	1.519 (3)
C9—O9	1.243 (3)	1.246 (3)	1.232 (3)
C9—N22	1.331 (3)	1.326 (3)	1.326 (3)
N22—C23	1.461 (3)		
N22—C24		1.454 (4)	
N22—C26			1.464 (3)
C21—C22	1.494 (3)	1.498 (4)	1.500 (2)
C21—O211	1.326 (3)	1.312 (4)	1.320 (3)
C21—O212	1.215 (3)	1.206 (4)	1.200 (3)
C22—C23	1.520 (3)	1.507 (4)	1.519 (3)
C23—C24		1.519 (4)	1.524 (2)
C24—C25			1.516 (2)
C25—C26			1.519 (2)
C2—N1—C71	108.9 (2)	108.9 (3)	108.9 (2)
N1—C2—C3	110.3 (2)	110.8 (2)	110.6 (2)
C2—C3—C8	127.6 (2)	127.4 (2)	127.9 (2)
C2—C3—C31	106.3 (2)	106.3 (2)	106.0 (2)
C31—C3—C8	126.0 (2)	126.2 (2)	126.1 (2)
C3—C31—C71	107.0 (2)	106.7 (2)	107.1 (2)
C3—C31—C4	133.6 (2)	134.4 (2)	134.1 (2)
C4—C31—C71	119.4 (2)	118.9 (2)	118.8 (2)
C31—C4—C5	118.3 (2)	119.1 (3)	118.7 (2)
C4—C5—C6	121.1 (2)	121.5 (3)	120.9 (2)
C5—C6—C7	121.9 (2)	121.2 (3)	121.8 (2)
C6—C7—C71	117.0 (2)	117.6 (3)	117.1 (2)
C31—C71—C7	122.3 (2)	121.7 (2)	122.6 (2)
N1—C71—C7	130.3 (2)	130.9 (3)	130.0 (2)
N1—C71—C31	107.4 (2)	107.4 (2)	107.4 (2)
C3—C8—C9	117.3 (2)	113.1 (2)	116.0 (2)
C8—C9—N22	117.9 (2)	116.2 (2)	116.5 (2)
C8—C9—O9	119.8 (2)	121.3 (2)	121.0 (2)
O9—C9—N22	122.2 (2)	122.4 (2)	122.5 (2)
C9—N22—C23	122.6 (2)		
C9—N22—C24		124.0 (2)	
C9—N22—C26			125.1 (2)
N22—C23—C22	111.0 (2)		
N22—C24—C23		112.1 (2)	
N22—C26—C25			112.0 (2)
C22—C21—O212	123.8 (2)	124.9 (3)	125.4 (2)
C22—C21—O211	113.3 (2)	112.9 (2)	111.8 (2)
O211—C21—O212	123.0 (2)	122.1 (3)	122.7 (2)
C21—C22—C23	112.6 (2)	114.3 (2)	115.1 (2)
C22—C23—C24		112.6 (2)	110.8 (2)
C23—C24—C25			114.1 (2)
C24—C25—C26			112.9 (2)

Table 4. *Selected torsion angles* (°) *for N-(IAA)-β-Ala* (1), *N-(IAA)-γ-Abu* (2), *N-(IAA)-δ-Ava and N-(IAA)-ε-Ahx* (3)

	(1)	(2)	*N*-(IAA)-δ-Ava	(3)
C2—C3—C8—C9	−118.4 (2)	−94.3 (4)	−93.5 (6)	−108.8 (2)
C31—C3—C8—C9	63.7 (3)	82.3 (3)	87.5 (6)	70.1 (3)
C3—C8—C9—O9	−163.3 (2)	45.1 (4)	47.6 (7)	−166.0 (2)
C3—C8—C9—N22	19.3 (3)	−137.6 (3)	−135.5 (3)	13.9 (3)
C23—C22—C21—O211	175.6 (2)	−175.0 (2)	170.8 (5)	−176.7 (2)
C23—C22—C21—O212	−5.4 (3)	2.2 (4)	−10.5 (8)	1.2 (3)

Orientation of the peptide NH towards the indole plane is observed in the structures of *N*-(IAA)-β-Ala (1) and *N*-(IAA)-ε-Ahx (3) (Table 4), and in crystal structures of IAA conjugates with α-amino acids (Kojić-Prodić, Nigović, Horvatić *et al.*, 1991). In the crystal structures of *N*-(IAA)-γ-Abu (2) and *N*-

Table 5. *Hydrogen bonds*

		D—H···*A* (Å)	*D*—H (Å)	H···*A* (Å)	*D*—H···*A* (°)	Symmetry operations on *A*
N-(IAA)-β-Ala (1)	N1—H···O212	2.854 (2)	0.95 (3)	1.91 (3)	175 (2)	$x, y, z-1$
	O211—H···O9	2.599 (2)	0.89 (3)	1.72 (3)	167 (2)	$x-\frac{1}{2}, y, -z+\frac{3}{2}$
N-(IAA)-γ-Abu (2)	N1—H···O212	2.869 (4)	1.01 (4)	1.91 (4)	158 (4)	$x-1, y+1, z$
	O211—H···O9	2.667 (3)	0.95 (4)	1.79 (4)	152 (4)	$x+\frac{1}{2}, \frac{3}{2}-y, 2-z$
	N22—H···O9	3.078 (3)	1.01 (5)	2.08 (5)	171 (3)	$x+1, y, z$
N-(IAA)-δ-Ava*	N22—H···O9	2.987 (6)	1.01 (5)	1.99 (5)	168 (5)	$x, y-1, z$
	O211—H···O9	2.663 (5)	0.98 (8)	1.69 (8)	172 (8)	$-x, -y, -z$
N-(IAA)-ε-Ahx (3)	N1—H···O212	2.854 (3)	0.99 (1)	1.94 (1)	153 (1)	$x, y+1, z$
	O211—H···O9	2.650 (2)	1.02 (1)	1.71 (1)	150 (1)	$x-1, y-1, z-1$

* Data for *N*-(IAA)-δ-Ava are from Kojić-Prodić, Nigović, Horvatić *et al.* (1991).

(IAA)-δ-Ava (Kojić-Prodić, Nigović, Horvatić *et al.*, 1991) the rotation about the C8—C9 bond occurs in such a way that O9—C—NH lies astride the indole plane. In the crystalline state this orientation is due to participation of the peptide group in the intermolecular hydrogen bond N22—H···O9 (Table 5). This type of H bond is not common and in most conjugate structures the peptide carbonyl group acts as the acceptor for the H atom of a carboxylic group. The peptide NH remains free and is shielded inside the hydrophobic pocket formed by the aromatic system and the aliphatic chain (Fig. 3). In the

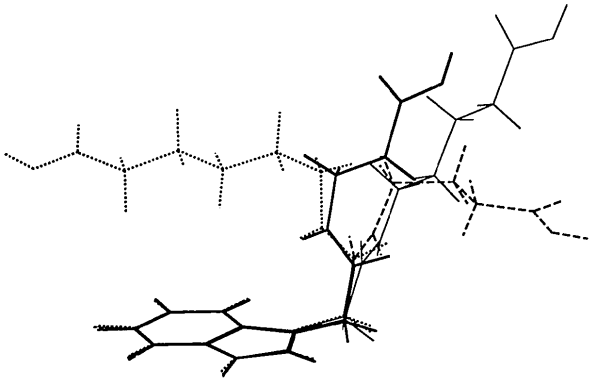


Fig. 4. Overlap diagrams of molecular conformations of IAA-conjugates: *N*-(IAA)-β-Ala (heavy line), *N*-(IAA)-γ-Abu (dashed line), *N*-(IAA)-δ-Ava (light line) and *N*-(IAA)-ε-Ahx (dotted line).

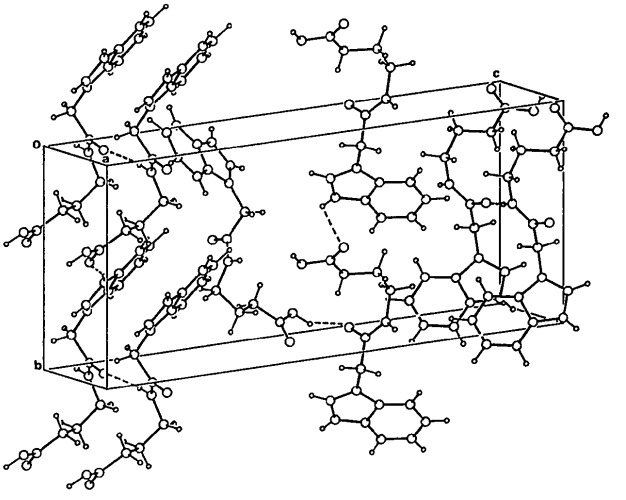


Fig. 6. Crystal packing with hydrogen bonds of *N*-(IAA)-γ-Abu (2).

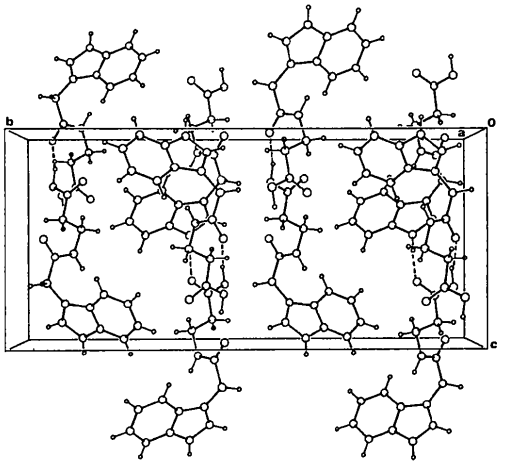


Fig. 5. Crystal packing with hydrogen bonds (dashed lines) of *N*-(IAA)-β-Ala (1).

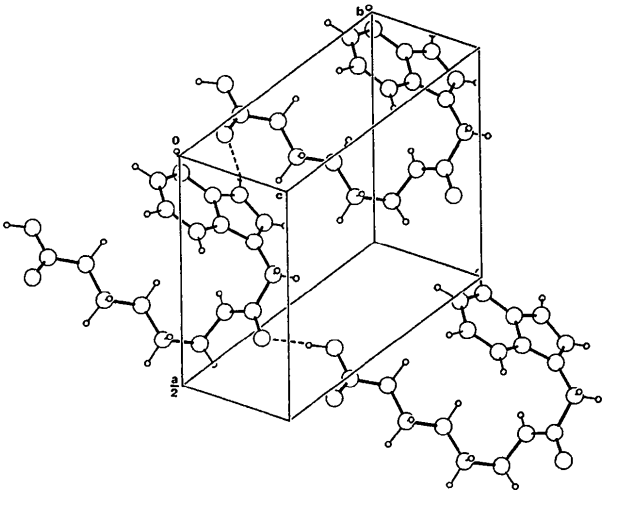


Fig. 7. Crystal packing with hydrogen bonds of *N*-(IAA)-ε-Ahx (3).

α-amino-acid conjugates the amphipatic character is more pronounced than in an ω-amino acid.

Crystal packing is predominantly determined by intermolecular hydrogen bonds (Table 5, Figs. 5, 6 and 7). Three different types of hydrogen bonds were observed. In the crystal structures of *N*-(IAA)-β-Ala (1) (Fig. 5), *N*-(IAA)-γ-Abu (2) (Fig. 6) and *N*-(IAA)-ε-Ahx (3) (Fig. 7) the indole N atom acts as a donor to the carboxylic O atom. This type of interaction was not detected in the structure of *N*-(IAA)-δ-Ava (Kojić-Prodić, Nigović, Horvatić *et al.*, 1991). The hydroxyl group of the carboxylic moiety is a proton donor to the peptide O atom; hydrogen bonds of the type O—H···O were observed in all structures of the ω-amino-acid conjugates. Hydrogen bonds between the peptide groups were detected in the structures of *N*-(IAA)-γ-Abu (2) and *N*-(IAA)-δ-Ava (Kojić-Prodić, Nigović, Horvatić *et al.*, 1991). This type of hydrogen bond affects the relative orientation of peptide group towards the indole moiety (Fig. 2). The crystal structure of *N*-(IAA)-γ-Abu (2) is the only one exhibiting all three types of hydrogen bonds.

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A Test of Chlorine and Fluorine Nonbonded Potential Functions with Lattice-Dynamical Calculations

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(*Received* 10 *August* 1991; *accepted* 3 *December* 1991)

Abstract

A lattice-dynamical calculation of vibrational frequencies and thermal parameters has been carried out in the harmonic approximation for chloro- and fluorohydrocarbons using the Born–von Kármán formalism in terms of molecular rotations and translations. Several empirical atom–atom potential functions from the literature were considered with or without explicit Coulombic terms. Their performance is analyzed by a comparison between the results of the calculations and experimental data.

0108-7681/92/030302-05$06.00

Introduction

The atomic displacement parameters which are routinely obtained from a crystal structure determination by diffraction methods may be considered simply as adjustable parameters in the least-squares process. They, however, carry information about the mean atomic displacements which may be useful for correcting bond distances using a rigid-body model (Schomaker & Trueblood, 1968), or to detect the directions of preferred molecular displacements. A review of the meaning and use of displacement